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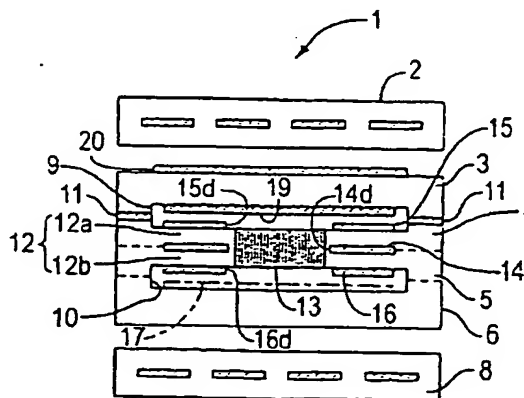
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(54) Gas sensor

(57) A gas sensor 1 having the following constituent features: (1) first processing space 9: a measurement gas which can be an exhaust gas is introduced thereinto via a first gas passage 11; (2) second processing space 10: a gas contained in the first processing space 9 is introduced thereinto via a second gas passage 13; (3) oxygen concentration detection element 4: adapted to measure the oxygen concentration of gas contained in the first processing space 9; (4) first oxygen pumping element 3: adapted to reduce the oxygen concentration of the exhaust gas introduced into the first processing space 9 within a range such that water vapor contained in the measurement gas is not substantially decomposed; (5) oxidation catalyst section 16: adapted to accelerate combustion of a combustible gas component contained in gas introduced into the second processing space 10 from the first processing space 9; and (6) combustible gas component concentration information generation/output section 5: having an output which varies according to the amount of oxygen consumed by combustion of the combustible gas component contained in the gas introduced into the second processing space 10, thereby providing information regarding the concentration of the combustible gas component of the exhaust gas. Also disclosed is a gas sensor system including the above gas sensor and first oxygen pumping operation control means for adjusting the oxygen concentration of the measurement gas introduced into

the first processing space within a range such that water vapor contained in the measurement gas is not substantially decomposed.

FIG. 2



With the recent tendency to tighten exhaust gas regulations for air pollution control, internal combustion engines such as gasoline engines, diesel engines and like engines tend to shift to a lean-burn operation in order to suppress generation of HC associated with incomplete combustion. An exhaust gas produced under lean-burn conditions has an oxygen concentration higher than that produced under stoichiometric or rich conditions. When the above-described conventional apparatus is applied to such an exhaust gas, an oxygen pumping element is significantly burdened in order to reduce the oxygen concentration to the above-mentioned low value. As a result, the service life of the oxygen pumping element is shortened. Furthermore, since the operating power of the oxygen pumping element must be increased, a high output peripheral control circuit must also be used which in turn increases the apparatus cost.

[0008] It is therefore the object of the present invention to provide a gas sensor and a method of manufacturing the gas sensor in which accuracy in measuring a combustible gas component concentration is less susceptible to decomposition of water vapor and which is suitably applicable to lean-burn conditions, as well as to provide a gas sensor system using the gas sensor.

[0009] The above object of the present invention is achieved by providing a gas sensor according to independent claim 1, a gas sensor system according to independent claim 29, and a method according to independent claim 27. Further advantageous features and aspects of the invention will be derivable from the dependent claims, the description and the appended drawings. The claims are to be understood as a first, non limiting approach to define the present invention in general terms. The inventive gas sensor may have the following characteristic features.

(1) First processing space: A first processing space is provided which is isolated from the surrounding environment. A gas to be measured (hereinafter referred to as a "measurement gas") is introduced into the first processing space via a first gas passage.

(2) Second processing space: A second processing space is provided which is isolated from the surrounding environment. A gas contained in the first processing space is introduced into the second processing space via a second gas passage.

(3) Oxygen concentration detection element: Adapted to measure the oxygen concentration of gas contained in the first processing space.

(4) First oxygen pumping element: Formed of an oxygen-ion conductive solid electrolyte. Electrodes are formed on opposing surfaces of the oxygen pumping element. The first oxygen pumping element pumps out oxygen from the first processing space or pumps oxygen into the first processing space so as to adjust the oxygen concentration of

the measurement gas introduced into the first processing space and measured by the oxygen concentration detection element. In this manner, the oxygen concentration preferably falls within a range such that water vapor contained in the measurement gas is not substantially decomposed, that is, within a range which does not substantially initiate a reaction of decomposing water vapor contained in the measurement gas.

(5) Oxidation catalyst element: Adapted to accelerate combustion of a combustible gas component contained in the gas which has been introduced into the second processing space from the first processing space via the second gas passage.

(6) Combustible gas component concentration information generation/output section: Adapted to have an output which varies according to the amount of oxygen consumed by reaction of the combustible gas component contained in the gas introduced into the second processing space, to thereby provide information regarding the concentration of the combustible gas component of the measurement gas.

[0010] The present invention also provides a gas sensor system having the following characteristic features.

(A) Gas sensor: Configured to have the following constituent features.

(1) First processing space: A first processing space is provided which is isolated from the surrounding environment. A measurement gas is introduced into the first processing space via a first gas passage.

(2) Second processing space: A second processing space is provided which is isolated from the surrounding environment. A gas contained in the first processing space is introduced into the second processing space via a second gas passage.

(3) Oxygen concentration detection element: Adapted to measure the oxygen concentration of gas contained in the first processing space.

(4) First oxygen pumping element: Formed of an oxygen-ion conductive solid electrolyte. Electrodes are formed on opposing surfaces of the oxygen pumping element. The first oxygen pumping element pumps out oxygen from the first processing space or pumps oxygen into the first processing space.

(5) Oxidation catalyst element: Adapted to accelerate combustion of a combustible gas component contained in a gas having an oxygen concentration which has been adjusted by the first oxygen pumping element and then introduced into the second processing space from the first processing space via a second

gen concentration of  $10^{-20}$  atm to  $10^{-14}$  atm as conventionally required, the first oxygen pumping element has a smaller burden even when measuring, for example, under lean-burn conditions. Thus, the service life of the oxygen pumping element is enhanced. Also, the power required to operate the oxygen pumping element is not very high, and a control circuit and other peripheral devices can be provided at low cost. Also, in this case, the first oxygen pumping element (or the oxygen pumping control means) is preferably configured such that the oxygen concentration of a measurement gas introduced into the first processing space and measured by the oxygen concentration detection element is adjusted such that the oxygen concentration falls within a range such that water vapor contained in the measurement gas is not substantially decomposed.

[0017] When the oxygen concentration of a measurement gas introduced into the first processing space becomes less than  $10^{-12}$  atm, decomposition of water vapor, if contained therein, becomes conspicuous. As a result, hydrogen generated by decomposition of water vapor may significantly impair accuracy in measuring a combustible gas component concentration. By contrast, when the oxygen concentration of the first processing space is in excess of  $10^{-6}$  atm, combustion of a combustible gas component becomes conspicuous in the first processing space. Accordingly, the combustible gas component concentration of a gas introduced into the second processing space becomes small with a potential failure to attain a predetermined measurement accuracy. More preferably, the oxygen concentration of the first processing space is adjusted to a value of  $10^{-11}$  atm to  $10^{-9}$  atm.

[0018] For example, when the gas sensor is set at a working temperature of  $600^{\circ}\text{C}$  to  $800^{\circ}\text{C}$  and the water vapor concentration of a measurement gas varies within a range of about 5% to 15%, oxygen that maintains equilibrium with water vapor and hydrogen has a minimum partial pressure of about  $10^{-12}$  atm. When the partial pressure of oxygen drops below the minimum value, decomposition of water vapor progresses, thereby affecting accuracy in measuring a combustible gas component concentration. Therefore, in this case, the oxygen concentration of the first processing space is preferably set to a value greater than the above minimum partial pressure of oxygen.

[0019] As used herein, unless specifically described otherwise, the oxygen concentration within the first processing space means the oxygen concentration measured by the oxygen concentration detection element. For example, when a part of a combustible gas component contained in a measurement gas burns and consumes oxygen, the oxygen concentration detected by the oxygen concentration detection element is not necessarily equal to the oxygen concentration before the consumption of oxygen as a result of combustion. Also, the oxygen concentration may vary at locations within the first processing space due to the presence of

a porous electrode disposed to face the first processing space which catalyzes combustion of a combustible gas component, or due to oxygen pumping of the oxygen pumping element. In this case as well, the oxygen concentration as measured by the oxygen concentration detection element is considered to represent the oxygen concentration within the first processing space. When the oxygen concentration of a measurement gas introduced into the first processing space is relatively high, the first oxygen pump operates to mainly pump oxygen out from the first processing space in order to cause the oxygen concentration as measured by the oxygen concentration detection element to fall within the range of  $10^{-12}$  -  $10^{-6}$  atm. By contrast, the first oxygen pump operates to pump oxygen into the first processing space when an increased amount of a combustible gas component (e.g., carbon monoxide, hydrogen, ammonia) burns while the first electrode, described below, is used as a catalyst for combustion, and oxygen consumption due to the combustion proceeds.

[0020] The present invention will in the following be described in detail with reference to the figures, in which

FIG. 1 is a front view showing an embodiment of a gas sensor of the present invention, a plane view, a sectional view taken along line B-B, a sectional view taken along line C-C, and a sectional view taken along line D-D.

FIG. 2 is a sectional view taken along line A-A of FIG. 1.

FIG. 3(a) is a sectional view showing an example of a connection between an electrode lead and a terminal, and FIG. 3(b) is a sectional view showing a modification of the gas sensor of FIG. 1.

FIGS. 4(a) and (b) are explanatory views illustrating a process of forming a processing space in the gas sensor of FIG. 1.

FIGS. 5(a) and (b) are explanatory views illustrating the process of forming the processing space in the gas sensor of FIG. 1.

FIG. 6 is a block diagram showing a circuit configuration example of a gas sensor system 50 using the gas sensor of FIG. 1.

FIG. 7 is an explanatory diagram showing an example of the contents of a concentration conversion table.

FIG. 8 is a flow chart showing a process flow of a control program of the gas sensor system 50 of FIG. 6.

FIGS. 9(a) and 9(b) are schematic diagrams showing two applications of the gas sensor of the present invention.

FIG. 10 is a sectional view showing another modification of the gas sensor of FIG. 1.

FIG. 11 is a block diagram showing a circuit configuration example of a gas sensor system 50 using the gas sensor of FIG. 10.

FIG. 12 is a graph showing the methane concentra-

another preferred embodiment, the combustible gas component concentration information generation/output section generates the combustible gas component concentration detection information on the basis of the concentration cell electromotive force developed by the second oxygen concentration cell element.

[0024] In the above configuration, the oxygen concentration within the second processing space is measured by means of the second oxygen concentration cell element. Since the concentration cell electromotive force of the second oxygen concentration cell element changes depending on the amount of oxygen consumed by combustion of the combustible gas component, the combustible gas component concentration information generation/output section can easily generate the combustible gas component concentration detection information based on the concentration cell electromotive force. Furthermore, the first electrode has an oxidation-related catalytic activity that is lower than that of the third electrode. Thus, at least a portion of a residual combustible gas component which has not been burned in the first processing space can be reliably burned in the second processing space, thereby improving sensor sensitivity. Also, since the electrode (third electrode) of the second concentration cell element exposed to the second processing space also serves as an oxidation catalyst section, the structure of the gas sensor or the gas sensor system is further simplified.

[0025] In the gas sensor of the present invention, a more preferable result is obtained by employing an electrode having the following structure. Specifically, a first oxygen pumping element comprises an oxygen-ion conductive solid electrolyte having seventh and eighth electrodes formed on opposing surfaces thereof, and the seventh electrode is disposed so as to be exposed to the first processing space. When the component to be detected is CO or HC, the seventh electrode is preferably composed of two layers, namely, a porous main electrode layer and a porous surface electrode layer. The porous main electrode layer is made of a Pt-Au alloy (Au content: 1 wt.% or less) or Pt. The porous surface electrode layer covers the main electrode layer to thereby form a surface layer portion of the seventh electrode. The surface electrode layer is made of a material selected from the group consisting of a metal containing Au or Ag as a main component, a Pt-Au alloy, an Au-Pd alloy, a Pt-Ag alloy and a Pt-Ni alloy (hereinafter collectively referred to as an "inactive metal"). The seventh electrode preferably has an oxidation-related catalytic activity toward the combustible gas component that is lower than that of the third electrode or lower than that of the third and fifth electrodes. As used herein, the term "X-Y alloy" means an alloy in which a metal component having the highest content by weight is X, and a metal component having the second highest content by weight is Y. The alloy may be an X-Y binary system alloy or a higher-order system alloy containing X, Y and other alloy components.

[0026] Materials for the electrodes of the oxygen concentration cell element or the oxygen pumping element must have a sufficient catalytic activity for desorption and recombination of oxygen molecules. Pt single metal, for example, is an excellent material in this point. However, if this material is used for the electrode exposed to the first processing space, the material has an extremely high combustion catalytic activity toward a combustion gas component. Therefore, the catalytic activity must be decreased slightly. For example, as conventionally practiced, Au, whose combustion catalytic activity is low, is mixed with Pt in an amount of up to about 20 wt.%, thereby forming a Pt-Au alloy. However, when the Au content increases, a considerable decrease in activity for desorbing oxygen molecules occurs concurrently with a decrease in the combustion catalytic activity toward a combustible gas component. Therefore, these two catalytic activities are difficult to balance.

[0027] This problem can be solved by employing the above-described multilayer electrode, in which the surface of the porous main electrode layer formed of a Pt-Au alloy or Pt having a high activity for desorbing oxygen molecules is covered with the porous surface electrode layer formed of an inactive metal having a low combustion catalytic activity toward a combustible gas component. This structure allows for a convenient adjustment to decrease the combustion catalytic activity toward a combustible gas component to the extent possible, while maintaining a sufficient level of oxygen molecule desorption activity.

[0028] In the present invention, the surface electrode layer is preferably formed of an Au-containing porous metal that has a considerably low combustion catalytic activity toward CO or HC and some degree of catalytic activity for desorption and recombination of oxygen molecules. Alternatively, a porous metal containing Ag as a main component, a porous Pt-Au alloy (Au content: 5 wt.% or more), a porous Pt-Pb alloy (Pb content: 1 wt.% or more), a porous Pt-Ag alloy (Ag content: 1 wt.% or more), a porous Pt-Ni alloy (Ni content: 1 wt.% or more), and the like may be used.

[0029] The surface electrode layer and the main electrode layer may be arranged such that these layers are in indirect contact with each other via one or more other layers. However, the use of a two-layer structure comprising the main electrode layer and the surface electrode layer simplifies the manufacturing process. In this case, when the surface electrode layer is formed of an Au-containing porous metal that contains Au as a main component, the remarkable effect of suppressing the combustion catalytic activity toward a combustible gas component can be obtained, while a sufficient level of oxygen molecule desorption activity is also maintained.

[0030] The above-described multilayer electrode is advantageously employed as the seventh electrode of the oxygen pump which does not require a sharp response to oxygen concentration. The above-

from the surface electrode layer into the main electrode layer so that Au constituting the main electrode layer is converted into a Pt-Au alloy. If the diffusion of the material of the surface electrode layer into the main electrode layer proceeds excessively, the thickness of the surface electrode layer becomes insufficient, or in an extreme case, the surface electrode layer disappears. For example, when the surface electrode layer is desirably formed mainly of Au and the main electrode layer is desirably formed mainly of Pt, the temperature for secondary firing is preferably set to about 800 - 1050°C in order to prevent excessive diffusion of Au into the main electrode layer. When the secondary firing temperature is less than 800°C, firing of the surface electrode layer becomes insufficient with the possibility of delamination of the surface electrode layer occurring due to insufficiently close contact. By contrast, when the secondary firing temperature is greater than 1050°C, the thickness of the surface electrode layer becomes insufficient due to diffusion of the Au component, or firing proceeds excessively, so that the porous structure is lost. In this case, the oxygen permeability that the porous electrode must have becomes difficult to maintain. When Au is mixed in the constituent metal of the main electrode layer in an amount of about 3 - 10 wt.% (for example, 10 wt.%) from the beginning, the diffusion of Au from the surface electrode layer into the main electrode layer can be suppressed because the extent of solid solution formation of Au into Pt is relatively small (about 5 wt.%) at 800°C. Thus, the drawbacks such as a reduction in thickness of the surface electrode layer can be effectively avoided.

[0036] The manufacturing method comprising the above-described secondary firing step can be performed efficiently in a preferred embodiment, when the gas sensor of the present invention is constructed such that a pumping cell unit including the first oxygen pumping element is formed separately from a sensor cell unit including the oxygen concentration detection element, the second processing space and the combustible gas component concentration information generation/output section; and the pumping cell unit and the sensor cell unit are joined and integrated with each other via a bonding material. In this case, the pumping cell unit is manufactured by firing such that the substrate electrode layer is formed without formation of the surface electrode layer; the secondary firing is performed in order to form the surface electrode layer on the substrate electrode layer of the pumping cell unit; and the pumping cell unit is integrated with the sensor cell unit, which has been separately manufactured by firing. Thus, the gas sensor is obtained. Preferably, a pump-cell-side fitting portion is formed in the pumping cell unit, and a sensor-cell-side fitting portion for engaging the pump-cell-side fitting portion is formed in the sensor cell unit. In this case, positioning during joining can be easily performed by engaging the pump-cell-side fitting portion and the sensor-cell-side fitting portion. Thus, the manufacturing

efficiency of the sensor can be improved.

[0037] The first and second oxygen concentration cell elements may be formed of an oxygen-ion conductive solid electrolyte composed mainly of  $ZrO_2$  ( $ZrO_2$  solid electrolyte). In the oxygen concentration cell element formed of a  $ZrO_2$  solid electrolyte, one electrode is in contact with a gas to be measured, which gas contains oxygen and a combustible gas component, while the other electrode is in contact with a reference atmosphere having a constant oxygen concentration. The electromotive force of the oxygen concentration cell element varies abruptly when the gas composition falls outside a stoichiometric composition in which oxygen and a combustible gas component are present in a proper ratio so that they completely react with each other. When an ordinary gasoline engine or diesel engine is operated under lean-burn conditions, a measurement gas emitted from the engine contains combustible gas components in a total concentration of about 0 to 1000 ppmC (ppmC: parts per million carbon equivalent). A measurement gas having such a combustible gas component concentration is introduced into the first processing space, and the oxygen concentration of the introduced measurement gas is adjusted to  $10^{-7}$  atm (preferably  $10^{-9}$  atm) or lower, as described previously. As a result, a gas introduced into the second processing space from the first processing space has a stoichiometric composition or a composition shifted slightly toward a rich condition. Thus, the output from the second oxygen concentration cell element is increased, thereby improving the sensitivity of the gas sensor.

[0038] As described above, the concentration cell electromotive force of the second oxygen concentration cell element changes depending on the amount of oxygen consumed by combustion of the combustible gas component. Therefore, in another preferred embodiment, the concentration cell electromotive force output provides the combustible gas component concentration detection information. In this case, the second oxygen concentration cell element serves as the combustible gas component concentration information generation/output section. In some cases, the above-described concentration cell electromotive force does not change linearly with the concentration of the combustible gas component. In such a case, the gas sensor system may be provided with an output conversion section having the following structure. Specifically, the output conversion section includes electromotive force-concentration relation storage means, concentration determination means and concentration value output means. The electromotive force-concentration relation storage means stores information regarding the relationship between the concentration cell electromotive force and the combustible gas component concentration. The concentration determination means determines a combustible gas component concentration corresponding to the concentration cell electromotive force output from the second oxygen concentration cell element, based

posed between the third electrode and the oxygen reference electrode constitute the second oxygen concentration cell element. Furthermore, the first oxygen pumping element is arranged opposite the partition wall with the first processing space disposed therebetween. This arrangement enables the two oxygen concentration cell elements to share the oxygen reference electrode, thereby implementing a compact sensor. When the second oxygen pumping element is provided, the second oxygen pump in another preferred embodiment is arranged opposite the partition wall with the second processing space disposed therebetween.

[0043] As described above, and in reference to FIG. 10, the first oxygen concentration cell element is defined as comprising an oxygen-ion conductive solid electrolyte having first (15) and second (14) electrodes formed on opposing surfaces thereof. The second oxygen concentration cell element is defined as comprising an oxygen-ion conductive solid electrolyte having third (16) and fourth (14) electrodes formed on opposing surfaces thereof. The first oxygen pumping element is defined as comprising an oxygen-ion conductive solid electrolyte having seventh (19) and eighth (20) electrodes formed on opposing surfaces thereof. The second oxygen pumping element is defined as comprising an oxygen-ion conductive solid electrolyte having fifth (17) and sixth (18) electrodes formed on opposing surfaces thereof. Electrode 15 is exposed to the first processing space, whereas electrodes 16 and 17 are exposed to the second processing space. Furthermore, some of these electrodes may have a dual function. For example, in reference to FIG. 10, electrode 14 which is an oxygen reference electrode serves as both the second and fourth electrodes.

[0044] Various embodiments of the present invention will now be described with reference to the drawings and Examples. However, the present invention should not be construed as being limited thereto, but as defined by the claims.

#### First Embodiment:

[0045] FIG. 1 shows a gas sensor 1 according to an embodiment of the present invention. The gas sensor 1 includes a first heater 2, a first oxygen pumping element (hereinafter referred to as the "first pumping element") 3, a first oxygen concentration cell element (hereinafter referred to as the "first cell element") 4, a second oxygen concentration cell element (hereinafter referred to as the "second cell element") 5, a shield member 6, and a second heater 8. These elements of the gas sensor 1 are in the shape of an elongated sheet and arranged in layers in this order so as to be integrated into a single unit. In the present embodiment, a second oxygen pump, described below, is not provided. A first processing space 9 is formed between the first pumping element 3 and the first cell element 4. A second processing space 10 is formed between the second cell element 5

and the shield member 6.

[0046] The elements 3 to 5 and the shield member 6 are formed of a solid electrolyte having oxygen-ion conductivity. A typical example of such a solid electrolyte is a  $ZrO_2$  solid solution containing  $Y_2O_3$  or  $CaO$ . Another example is a solid solution of  $ZrO_2$  and an oxide of an alkaline earth metal or of a rare earth metal.  $ZrO_2$  serving as a base material may include  $HfO_2$ . The present embodiment employs a solid electrolyte ceramic of  $ZrO_2$  obtained through solid solution of  $Y_2O_3$  or  $CaO$ . The first and second heaters 2 and 8, respectively, are known ceramic heaters and are adapted to heat the elements 3 to 5 to a predetermined working temperature ( $650^\circ C$  to  $700^\circ C$ ). An insulating layer (not shown in FIG. 1; an insulating layer 260 is shown in FIG. 4) is interposed between the elements 3 to 5 and the shield member 6. The insulating layer is primarily formed of  $Al_2O_3$ . The laminated sensor structure is formed by laminating and subsequent firing of ceramic green sheets (ceramic moldings), which become the elements and members 3 to 6.

[0047] First gas passages 11 are formed at both side wall portions of the first processing space 9 so as to establish communication between the first processing space 9 and an external atmosphere to be measured. Located on both widthwise sides of the first processing space 9 as shown in FIG. 2, the first gas passages 11 are interposed between and extend along the first pumping element 3 and the first cell element 4 in a longitudinal direction of the elements 3 and 4. The first gas passage 11 is formed of a porous ceramic body having communicating pores, which ceramic body is a porous fired body of  $Al_2O_3$  or the like. Thus, the first gas passages 11 serve as diffusion-controlling passages for introducing a measurement gas into the first processing space 9 from the outside while a constant diffusion resistance is maintained.

[0048] The first cell element 4 and the second cell element 5 are arranged in adjacent layers. A partition wall 12, formed of an oxygen-ion conductive solid electrolyte, is interposed between the first processing space 9 and the second processing space 10. In other words, the first and second processing spaces 9 and 10, respectively, are arranged with the partition wall 12 interposed therebetween. A second gas passage 13 is formed in the partition wall 12 so as to establish communication between the first processing space 9 and the second processing space 10. An oxygen reference electrode 14 is embedded in the partition wall 12 at a thicknesswise intermediate portion. As in the case of the first gas passages 11, the second gas passage 13 is formed of a porous ceramic body and serves as a diffusion-controlling passage for introducing a gas into the second processing space 10 from the first processing space 9 while maintaining a constant diffusion resistance. The first and second gas passages 11 and 13, respectively, may assume the form of small holes or slits instead of being formed of a porous ceramic body (or a



the first processing space 9 by means of the bonding coat 269 serving as the insulating layer 260.

[0054] As shown in FIGS. 5(a) and 5(b), the support patterns 266a (266b) and the auxiliary support pattern 267a (267b) are complementarily formed to thereby form a substantial plane. When the green sheets 220 and 230 are superposed to each other as shown in FIG. 4(a), the reinforcing effect of the auxiliary support patterns 267a and 267b prevents or suppresses the collapse of the support patterns 266a and 266b butting against each other. As exaggeratedly shown in FIG. 4(a), even when the bonding coat 269 is made considerably thinner than the total thickness of the support patterns 266a and 266b, the green sheets 220 and 230 can be bonded together by means of the interposed bonding coat 269. Because the green sheets 220 and 230 are flexible, the bonding can be established through a slight flexure thereof. Thus, the green sheets 220 and 230 can be smoothly fired into a single unit.

[0055] As shown in FIG. 3(b), the first processing space 9 may be formed using a spacer 25 (that can be formed of a  $ZrO_2$  solid electrolyte ceramic) having a space 25a for forming the processing space 9. In this case, the spacer 25 is sandwiched between the first pumping element 3 and the first cell element 4, which are then fired for integration. Similarly, the second processing space 10 may be formed using a spacer 26 which has a similar space 26a and which is interposed between the second cell element 5 and the shield member 6.

[0056] Next, an embodiment of a gas sensor system using the gas sensor 1 above is described as follows.

[0057] FIG. 6 shows an example of an electrical block diagram of a gas sensor system (hereinafter referred to as the "sensor system") using the gas sensor 1. Specifically, the gas sensor system 50 includes the gas sensor 1, a microprocessor 52, and a peripheral circuit 51 for connecting the gas sensor 1 to the microprocessor 52. The microprocessor 52 is a main portion of an output conversion unit and includes an I/O port 56 serving as an input/output interface, a CPU 53, a RAM 54, a ROM 55, etc. The CPU 53, the RAM 54, the ROM 55 and the like are connected to the I/O port 56. The RAM 54 has a work area 54a for the CPU 53, and a storage area 54b for storing calculated values of component concentration. The ROM 55 contains a control program 55a and an HC concentration conversion table 55b. The control program 55a is used for controlling the gas sensor system 50 in computing a component concentration and in outputting the computed component concentration. The CPU 53 serves as concentration determination means, and determines a component concentration according to the control program 55a stored in the ROM 55. The I/O port 56 serves as the concentration value output means.

[0058] In the gas sensor system 50, the gas sensor 1 operates in the following manner. The exhaust gas sensor 1 is heated to a predetermined working temperature

by means of the first heater 2 and the second heater 8 shown in FIG. 2, etc. (either of the heaters may be omitted). The working temperature is a temperature at which the  $ZrO_2$  solid electrolyte forming elements 3 to 5 is activated. While the gas sensor 1 is heated at its working temperature, a measurement gas is introduced into the first processing space 9 through the first gas passages 11. The first cell element 4 measures the oxygen concentration of the introduced measurement gas. Based on the oxygen concentration detected by the first cell element 4, the first pumping element 3 pumps out oxygen from or pumps oxygen into the gas contained in the first processing space 9 so as to bring the oxygen concentration to a predetermined target value of  $10^{-12}$  atm to  $10^{-6}$  atm (preferably  $10^{-11}$  atm to  $10^{-9}$  atm), in other words, to a predetermined target value at which water vapor contained in the measurement gas is not substantially decomposed. Generally, the oxygen concentration of the measurement gas is higher than the above target value. In this case, the first pumping element 3 operates so as to mainly reduce the oxygen concentration of the first processing space 9. When the oxygen concentration detected by the first cell element 4 falls within the range of  $10^{-12}$  atm to  $10^{-6}$  atm, the corresponding concentration cell electromotive force of the first cell element 4 falls within the range of about 300 mV (corresponding to  $10^{-6}$  atm) - 600 mV (corresponding to  $10^{-12}$  atm).

[0059] After reducing the oxygen concentration to the above predetermined value, the gas contained in the first processing space 9 flows into the second processing space 10 through the second gas passage 13. Because the third electrode 16 has a higher oxidation-related activity than the first electrode 15 toward a combustible gas component such as HC or the like, a combustible gas component of the gas contained in the second processing space 10 is burned while the third electrode 16 serves as an oxidation catalyst. Thus, oxygen is consumed. The oxygen concentration of the second processing space 10 varies according to the oxygen consumption associated with the combustion, i.e., according to the concentration of a combustible gas component. Therefore, when the concentration is measured as the concentration cell electromotive force of the second cell element 5, the concentration of the combustible gas component contained in the measurement gas can be determined from the thus-measured concentration cell electromotive force.

[0060] On the surface of the shield member 6 disposed opposite to the partition wall 12 with the second processing space interposed therebetween, a porous metal layer 17 may be formed separately from the third electrode 16 so as to be exposed to the second processing space 10. The porous metal layer 17 may be formed of a metal, such as Pt, having a catalytic activity for the combustion of a combustible gas component which is higher than that of the electrodes 19 and 15. In this case, the porous metal layer 17, together with the

with the combustion. Thus, the concentration cell electromotive force output is utilized as information regarding the combustible gas component concentration of the measurement gas. By operation of the first pumping element 3, the oxygen concentration of the first processing space 9 is adjusted to a value such that water vapor contained in the measurement gas is not substantially decomposed. Even when the decomposition reaction is initiated, the degree of the reaction is very small. Thus, an impairment in accuracy in measuring a combustible gas component concentration is effectively prevented which would otherwise result from combustion of hydrogen generated from decomposition of water vapor.

[0067] Next, applications of the gas sensor 1 or the gas sensor system 50 will be described. FIG. 9(a) schematically shows an exhaust gas purification system of a gasoline engine. An oxygen sensor (1), a three way catalytic converter and a second oxygen sensor (2) are attached onto an exhaust pipe in this order starting from the engine side. The gas sensor 1 of the present invention is provided on the downstream side of the oxygen sensor (2). The oxygen sensor (1) is used for air-fuel ratio control. The three way catalytic converter concurrently performs oxidation of HC and reduction of NOx to thereby purify an exhaust gas, which is a measurement gas. The exhaust gas sensor (2) measures the oxygen concentration of the purified exhaust gas. The gas sensor 1 measures the HC concentration of the purified exhaust gas, for example, in order to judge whether the catalyst is deteriorated.

[0068] The oxygen concentration of the exhaust gas may be measured using the separately provided oxygen sensor (2). However, because the current flowing through the first oxygen pumping element 3 of the gas sensor 1 changes linearly in accordance with the oxygen concentration of the exhaust gas, information regarding the oxygen concentration of the exhaust gas may be obtained from the current. In this case, the oxygen sensor (2) may be omitted.

[0069] FIG. 9(b) schematically shows an exhaust gas purification system of a diesel engine. A light oil injection valve and an NOx decomposition catalyst are attached onto an exhaust pipe in this order starting from the engine side. The light oil injection valve is used for injecting light oil serving as an HC source into an exhaust gas. The NOx decomposition catalyst decomposes NOx into nitrogen and oxygen while using HC added through light oil injection as a reducer, thereby purifying the exhaust gas. The gas sensor 1 of the present invention is disposed on the upstream side of the NOx decomposition catalyst and monitors the HC concentration of the light-oil-injected exhaust gas in order to feedback-control the amount of light oil to be injected into the exhaust gas.

[0070] In the gas sensor 1, the first cell element 4 and the second cell element 5 are each formed of a ZrO<sub>2</sub> solid catalyst. In the case of an oxygen concentration

cell element formed of a ZrO<sub>2</sub> solid electrolyte and configured such that one electrode is in contact with a gas to be measured, which gas contains oxygen and a combustible gas component, whereas the other electrode is in contact with a reference atmosphere having a constant oxygen concentration, its electromotive force varies abruptly when the gas composition falls outside a stoichiometric composition in which oxygen and a combustible gas component are present in a proper ratio so that they completely react with each other. When an ordinary gasoline engine or diesel engine is operated under lean-burn conditions, an exhaust gas containing combustible gas components in a total concentration of about 0 to 1000 ppmC is emitted from the engine. An exhaust gas having such a combustible gas component concentration is introduced into the first processing space 9, and the oxygen concentration of the introduced exhaust gas is adjusted to 10<sup>-7</sup> atm (preferably 10<sup>-9</sup> atm) or lower as described above. As a result, a gas introduced into the second processing space 10 from the first processing space 9 has a stoichiometric composition or a composition shifted slightly toward a rich condition. Thus, the output electromotive force of the second cell element 5 is increased, thereby improving the sensitivity of the gas sensor 1.

[0071] In the gas sensor 1, as shown in FIGS. 1 and 10, a second oxygen pumping element (hereinafter referred to as the "second pumping element") 7 may be provided in place of the seal member 6 on the side of the second processing space 10. The structure of the second pumping element 7 is substantially the same as that of the first pumping element 3. An electrode 17 is formed on the surface exposed to the second processing space 10, and an electrode 18 is formed on the opposite surface. The electrode exposed to the second processing space 10 is referred to as the "fifth electrode 17".

[0072] In this case, the first pumping element 3 and the first cell element 4 form a main portion of the first processing space forming section, and the second cell element 5 and the second pumping element 7 form a main portion of the second processing space forming section. The operation of this exhaust gas sensor 1 is as follows. Unlike the above-described exhaust gas sensor in which the concentration cell electromotive force of the second cell element 5 is output as the oxygen concentration within the second processing space 10, the second pumping element 7 pumps oxygen into the second processing space 10 to compensate for a reduction of oxygen due to the combustion of the combustible gas component, so that the oxygen concentration within the second processing space 10 is made substantially constant. A pumping current (or a pumping voltage) at that time is output as the combustible gas component concentration detection information.

[0073] FIG. 11 shows the circuit diagram of the gas sensor system 50 in this case. The structure on the first processing space 9 side is completely the same as that



superposition.

[0078] As shown in FIG. 20(a), the seventh electrode 19 has a two-layer structure composed of a porous main electrode layer 151 and a porous surface electrode layer 152 that forms a surface portion of the seventh electrode 19. The main electrode layer 151 is formed of Pt or a Pt-Au alloy (in the present embodiment, substantially the entire portion is formed of Pt). The surface electrode layer 152 is formed of an Au-containing metal that contains Au as a main component (in the present embodiment, substantially the entire portion is formed of Au). The first electrode 15 shown in FIG. 19 is formed of a porous metal such as porous Pt or a porous Pt-Au alloy (Au content: not greater than 1 wt.%) (in the present embodiment, substantially the entire portion is formed of Pt) as in the case of the other electrodes.

[0079] Because the surface of the porous main electrode layer 51 formed of Pt, which has a high activity of desorbing oxygen molecules, is covered with the porous surface electrode layer 152 formed of Au, which has a low catalytic activity for combustion of a combustible gas component, the catalytic activity for combustion of the combustible gas component within the first processing space can be decreased, while the activity of desorbing oxygen molecules is maintained at a sufficient level. Thus, a loss of a combustible gas component such as HC to be detected can be prevented, so that the sensor sensitivity can be increased. In the case where substantially the entire portion of the main electrode layer 151 is formed of Pt and substantially the entire portion of the surface electrode layer 152 is formed of Au, the value of  $\{WAu/(WPt+WAu)\} \times 100$  preferably falls within the range of 2 - 20 wt.%, where WPt is the Pt content by weight of the seventh electrode 19, and WAu is the Au content by weight of the seventh electrode 19. When this value is less than 2 wt.%, the combustion catalytic activity of the seventh electrode 19 cannot be sufficiently decreased, with a possible result that the sensitivity of the sensor decreases. By contrast, when this value exceeds 20 wt.%, the catalytic activity of the seventh electrode 19 for desorption and recombination of oxygen molecules decreases excessively, with a possible result that the function of the oxygen pumping element 3 becomes insufficient. More preferably, the value falls within the range of 3 - 10 wt.%.

[0080] A method shown in FIG. 20(b) may be used to form the surface electrode layer 152 on the main electrode layer 151. That is, a paste containing particles of a material for the surface electrode layer 152 is applied onto the fired main electrode layer 151, and is then fired at a temperature lower than that for the firing of the main electrode layer 151. Alternatively, as shown in FIG. 20(c), the surface electrode layer 152 may be formed using vapor-phase film formation such as vacuum deposition or sputtering. As shown in FIG. 20 (b) and (c), because many voids are formed in the porous main electrode layer 151 in a complex manner, the surface

electrode layer 152 may not be formed such that its material fails to enter deeply into the voids P. In this case, parts of the main electrode layer 151 are not covered by the surface electrode layer 152 and remain exposed. However, because such exposed portions exhibit a strong catalytic activity for desorption and recombination of oxygen molecules, the formation of such exposed portions is rather preferable in terms of securing the function of the oxygen pumping element.

[0081] An example process for manufacturing the pumping cell unit 111 and the sensor cell unit 112 shown in FIG. 19 will be described with reference to FIGS. 21 and 22. FIG. 21 shows a laminate structure of a first unfired assembly 211 used for manufacturing the pumping cell unit 111. The first unfired assembly 211 includes a first portion 211a and a second portion 211b. The first portion 211a is mainly composed of a ZrO<sub>2</sub> green sheet (hereinafter also referred to as a green sheet) 220, which will become the first pumping element 3. The second portion 211b is mainly composed of a green sheet 231, which will serve as the spacer 25. The green sheet is formed by sheeting a kneaded mixture of a ZrO<sub>2</sub> powder, a forming aid such as an organic binder, and an organic solvent.

[0082] In the first portion 211a, by using an Al<sub>2</sub>O<sub>3</sub> paste or the like, insulating coats (insulating layer patterns) 221 and 222 for insulating the leads 20a and 19a from the first pumping element 3 are formed on the corresponding surfaces of the green sheet 220 in regions other than those corresponding to the electrodes 20 and 19 (hereinafter, for reference numerals or symbols see also FIG. 1, as needed, in addition to FIG. 19). After the insulating coats 221 and 222 are formed, electrode patterns 223 and 224a for forming the electrodes 20 and 19 (only a main electrode layer 151 for the electrode 19 (FIG. 20)) and the leads 20a and 19a are formed by printing using a Pt paste or the like. A protective over coat 225 is formed on the electrode pattern 223, which will serve as the outer electrode 20, using an Al<sub>2</sub>O<sub>3</sub> paste or the like. A pattern 226 of porous alumina paste or the like, which will serve as a first gas passage 11, is provided on the pattern 224b.

[0083] In the second portion 211b, insulating coats 230 and 232 are formed on the corresponding surfaces of the green sheet 231 in a manner similar to that used for the first portion 211a. A pattern 229, which will serve as a first gas passage 1.1, is formed on the insulating coat 230 using an Al<sub>2</sub>O<sub>3</sub> paste. Green sheets 234, which will serve as fitting projections 111a, are bonded onto the insulating coat 232 using bonding coats 233 (formed from alumina paste).

[0084] The first portion 211a and the second portion 211b are bonded together using a bonding coat 228, while end portions of Pt-Rh alloy wires 227a and 227b, which will serve as terminals of the electrodes 20 and 19, are sandwiched between the portions 211a and 211b. The thus-obtained first unfired assembly 211 is fired to obtain a pumping cell unit in which a surface

ically, the sensor output corresponding to either methane concentration remained almost unchanged for a water vapor concentration of 5% and 10%. This indicates that in the gas sensor 1, decomposition of water vapor is hardly initiated during measurement, and thus a stable methane concentration is obtained regardless of the water vapor concentration. As a Comparative Example, the target electromotive force EC of the first cell element 4 was set to a value (approximately 651 mV) such that the target oxygen concentration of the first processing space 9 was  $10^{-13}$  atm. In this state, an experiment was conducted in a manner similar to that of the above-described experiment. The result is shown in FIG. 15. As seen from FIG. 15, the sensor output was significantly influenced by the water vapor concentration.

#### Example 2:

[0093] Another experiment was conducted in a state in which the same exhaust sensor 1 as used in Example 1 was built in the exhaust gas sensor system 50 of FIG. 6. In this experiment, the test gas was composed of methane (0 ppmC or 500 ppmC), CO (0 - 500 ppmC), oxygen (7%), water vapor (10%), carbon dioxide (10%) and nitrogen (balance). The exhaust sensor 1 was held in the test gas and heated by heaters 2 and 8 so as to heat the elements 3 to 5 to a temperature of 650°C. The target electromotive force EC of the first cell element 4 was set to a value (about 550 mV) such that the target oxygen concentration of the first processing space 9 was  $10^{-11}$  atm. The sensor system 50 was operated under these conditions, and the concentration cell electromotive force of the second cell element 5 was measured as a sensor output. The result is shown in FIG. 17. As seen from FIG. 17, the sensor output corresponding to each methane concentration remained almost unchanged for any CO concentration. This demonstrates that the exhaust gas sensor 1 of the present invention stably provides a methane concentration detection output regardless of the CO concentration. FIG. 18 shows the result of a similar experiment which was performed using test gases each of which contained hydrogen (0 ppm or 500 ppm) or propane (0 ppm or 500 ppm) instead of methane and which also contained oxygen (7%), water vapor (10%), carbon dioxide (10%) and nitrogen (balance). The result of the experiment is shown in FIG. 18. From these results, it is seen that when a test gas does not contain methane gas, the sensor output is small and remains almost unchanged regardless of the hydrogen concentration or the propane concentration. The above-described result demonstrates that the exhaust gas sensor 1 of the present invention has excellent selectivity for detection of methane.

#### Example 3:

[0094] In the gas sensor 100 shown in FIG. 19 (for reference numerals or symbols see also FIG. 2), the porous electrodes 14 to 16 and 20 were formed using a Pt-Au (1% by weight) alloy. The seventh electrode 19 was a two-layered electrode composed of the main electrode layer 151 (FIG. 20) and the surface electrode layer 152. The main electrode layer 151 was integrally formed with the pumping cell unit 111 using a Pt-Au (1% by weight) alloy by firing. Au paste was applied onto the main electrode layer 151, followed by secondary firing (at 900°C) to thereby form the surface electrode layer 152. As in the case of Example 1, the first processing space 9 and the second processing space 10 each had a height of 0.02 mm, a width of 22 mm and a length of 7 mm. A section was taken across the thickness of the seventh electrode 19. The composition of the section was analyzed using an Electron Probe Micro Analyzer (EPMA; energy diffusion system). As a result, the Au content was found to be about 4.1% by weight when the total content of Au and Pt in the main electrode portion was taken as 100% by weight. It was confirmed that a surface electrode layer 152 mainly composed of Au was formed in a surface layer region of the main electrode portion.

[0095] The sensor 100 was incorporated into the gas sensor system 50 of FIG. 6. The sensor 100 was held in a test gas composed of oxygen (7%), water vapor (10%), carbon dioxide (10%), nitrogen monoxide (500 ppm), methane (200 ppmC) serving as a combustible gas component and nitrogen (balance). The sensor 100 was heated using heaters 2 and 8 (FIG. 1) so as to heat the elements 3 to 5 to a temperature of 750°C. In the gas sensor 100, the target electromotive force EC of the first oxygen concentration cell element 4 was set to a value (about 550 mV) such that the target oxygen concentration  $P_X$  of the first processing space 9 was  $10^{-11}$  atm. The sensor system 50 was operated under these conditions to examine how the electromotive force E of the second oxygen concentration cell element 5 varies with the methane concentration. The test revealed that the electromotive force E corresponding to a methane concentration of 200 ppmC in the gas sensor 100 was about 350 mV, which is larger than the value of about 240 mV observed with the sensor of Example 1. A conceivable reason for such an improvement in sensor sensitivity is that the above-described two-layered structure of the seventh electrode 19 facilitates combustion of methane to thereby reduce a loss associated with combustion of methane within the first processing space 9.

[0096] A section of the seventh electrode which was not used yet after secondary firing was examined using EPMA attached to an SEM. FIG. 23 shows characteristic X-ray images (about 1000 magnifications) of the section corresponding to Pt (FIG. 23(a)), Au (FIG. 23(b)) and Zr (FIG. 23(c)). In the images shown in FIG. 23, a brighter portion indicates a higher characteristic X-ray

a  $P_x$  value of  $10^{-6}$  atm or higher,  $I_D$  exhibited a sharp increase (i.e., a decrease in apparent combustible gas component concentration). It is considered that this is because methane was burned within the first processing space, i.e., the methane concentration was reduced due to excessive oxygen concentration.

## Claims

### 1. A gas sensor (1) comprising:

a first processing space (9) and a first gas passage (11) for introducing a measurement gas containing oxygen, water vapor and a combustible gas component into said first processing space (9);

a second processing space (10) and a second gas passage (13) for introducing a gas contained in said first processing space (9) into said second processing space (10);

an oxygen concentration detection element for measuring the oxygen concentration of gas contained in said first processing space (9);

a first oxygen pumping element (3) comprising an oxygen-ion conductive solid electrolyte having electrodes formed on opposing surfaces thereof, said first oxygen pumping element (3) pumping out oxygen from said first processing space (9) or pumping oxygen into said first processing space (9) so as to adjust the oxygen concentration of the measurement gas introduced into said first processing space (9) and measured by said oxygen concentration detection element within a predetermined range;

an oxidation catalyst for accelerating combustion of a combustible gas component contained in the gas which has been introduced into said second processing space (10) from said first processing space (9) via the second gas passage (13); and

a combustible gas component concentration information generation/output section for providing information regarding the concentration of the combustible gas component of the measurement gas, having an output which varies according to the amount of oxygen consumed by combustion of the combustible gas component contained in the gas introduced into said second processing space (10).

2. The gas sensor (1) according to claim 1, wherein said first oxygen pumping element (3) adjusts the oxygen concentration of the measurement gas such that water vapor contained in the measurement gas is not substantially decomposed;

3. The gas sensor (1) according to claim 1 or 2,

wherein said first oxygen pumping element (3) adjusts the oxygen concentration of the measurement gas within a range of  $10^{-12}$  atm to  $10^{-6}$  atm.

4. The gas sensor (1) according to any of the preceding claims, wherein said oxidation catalyst is for accelerating combustion of said combustible gas component which has been introduced into said second processing space (10) after adjusting the oxygen concentration within said range.

5. The gas sensor (1) according to any of the preceding claims, wherein said oxygen concentration detection element comprises a first oxygen concentration cell element (4) comprising an oxygen-ion conductive solid electrolyte having first (15) and second (14) electrodes formed on opposing surfaces thereof, said first electrode (15) being exposed to said first processing space (9).

6. The gas sensor (1) according to any of the preceding claims, further comprising a second oxygen concentration cell element (5) for measuring the oxygen concentration of gas contained in said second processing space (10).

7. The gas sensor (1) according to any of the preceding claims, further comprising a second oxygen concentration cell element (5) comprising an oxygen-ion conductive solid electrolyte having third (16) and fourth (14) electrodes formed on opposing surfaces thereof, said third electrode (16) being exposed to said second processing space (10), said second oxygen concentration cell element (5) developing an electromotive force depending on the oxygen concentration of the gas contained in said second processing space (10).

8. The gas sensor (1) according to claim 6 or 7, wherein said second oxygen concentration cell element (5) is comprised in said combustible gas component concentration information generation/output section.

9. The gas sensor (1) according to any of claims 5 to 8, wherein said first (15) and/or third electrodes (16) comprise a porous electrode having an oxygen molecule desorbent capability.

10. The gas sensor (1) according to any of claims 7 to 9, wherein said third electrode (16) serves as the oxidation catalyst.

11. The gas sensor (1) according to any of claims 7 to 10, wherein said first electrode (15) has an oxidation-catalytic activity that is lower than that of said third electrode (16).

formed on opposing surfaces thereof, said seventh electrode (19) being exposed to said first processing space (9);

the seventh electrode (19) comprises:  
 a porous main electrode layer (151) comprising a Pt-Au alloy or Pt; and  
 a porous surface electrode layer (152) covering the main electrode layer (151), said surface electrode layer (152) comprising a material selected from the group consisting of a metal containing Au or Ag as a main component, a Pt-Au alloy, an Au-Pd alloy, a Pt-Ag alloy and a Pt-Ni alloy,  
 wherein the seventh electrode (19) has a lower oxidation-catalytic activity than the third electrode (16) or the third (16) and fifth (17) electrodes.

22. The gas sensor (1) according to claim 21, wherein the seventh electrode (19) has a two-layer structure comprising:

a porous main electrode layer (151) comprising a Pt-Au alloy or Pt; and  
 a porous surface electrode layer (152) covering the main electrode layer (151), said surface electrode layer (152) comprising an Au-containing metal containing Au as a main component.

23. The gas sensor (1) according to any of claims 5 to 22, wherein said first electrode (15) comprises a porous metal comprising a Pt-Au alloy, a Pt-Ag alloy, or Pt.

24. The gas sensor (1) according to any of claims 21 to 23, wherein said first electrode (15) has an area that is smaller than that of said seventh electrode (19).

25. The gas sensor (1) according to any of the preceding claims, comprising a pumping cell unit (111) including said first oxygen pumping element (3) and a sensor cell unit (112) including said oxygen concentration detection element, said pumping cell unit (111) being arranged separately from said sensor cell unit (112), said second processing space (10) and said combustible gas component concentration information generation/output section; and said pumping cell unit (111) and said sensor cell unit (112) being joined and integrated with each other via a bonding material.

26. The gas sensor (1) according to claim 25, wherein said pumping cell unit (111) comprises a pump-cell-side fitting portion unit (111a), and said sensor cell unit (112) comprises a sensor-cell-side fitting por-

tion (112a) engaged with the pump-cell-side fitting portion (111a); and

said pumping cell unit (111) and said sensor cell unit (112) are joined and integrated with each other via engagement of the pump-cell-side fitting portion (111a) with the sensor-cell-side fitting portion (112a).

27. A method of manufacturing a gas sensor (1) of any of claims 21 to 26, said method comprising:

a substrate electrode layer forming step which comprises forming a substrate electrode pattern containing an unfired main electrode layer of material powder for the main electrode layer (151) of the seventh electrode (19) on an unfired solid electrolyte compact of the oxygen-ion conductive solid electrolyte layer constituting said first oxygen pumping element (3), and integrally firing the unfired main electrode layer (151) with the unfired solid electrolyte compact to form on the oxygen-ion conductive solid electrolyte layer a substrate electrode layer containing the main electrode layer (151); and  
 a surface electrode layer (152) forming step which comprises forming a layer of material powder for the surface electrode layer (152) on the substrate electrode layer, and subjecting to a secondary firing at a temperature lower than the integrally firing temperature to thereby form the surface electrode layer (152).

28. The manufacturing method according to claim 27, wherein said gas sensor (1) comprises a pumping cell unit (111) including said first oxygen pumping element (3) and a sensor cell unit (112) including said oxygen concentration detection element, said pumping cell unit (111) being arranged separately from said sensor cell unit (112), said second processing space (10) and said combustible gas component concentration information generation/output section; and said pumping cell unit (111) and said sensor cell unit (112) being joined and integrated with each other via a bonding material; and

said method comprises the steps of:  
 firing the substrate electrode layer without forming the surface electrode layer (152);  
 carrying out said secondary firing to form the surface electrode layer (152) on the substrate electrode layer of said pumping cell unit (111); and  
 integrating said pumping cell unit (111) with said sensor cell unit (112), which units have been separately manufactured through the firing steps.

FIG. 1

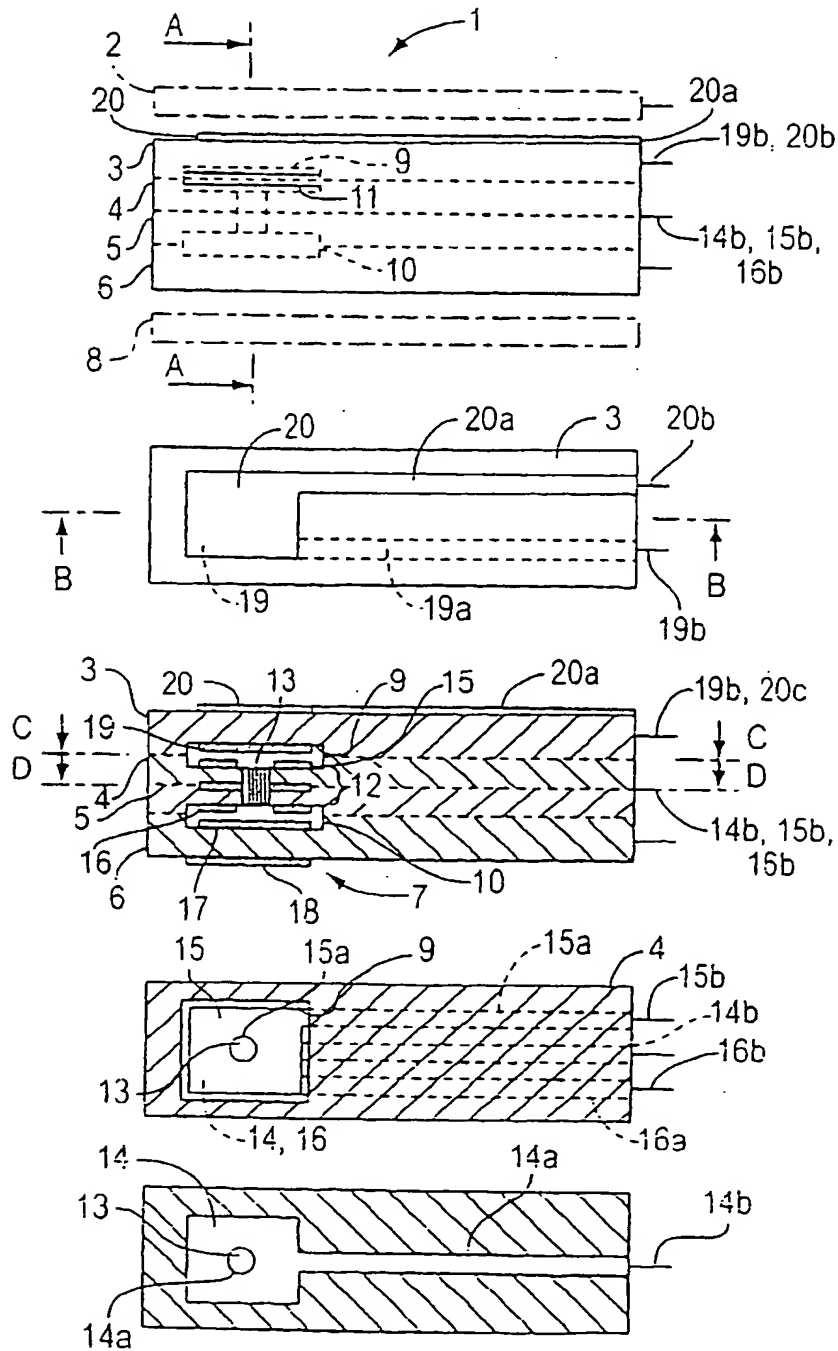


FIG. 3(a)

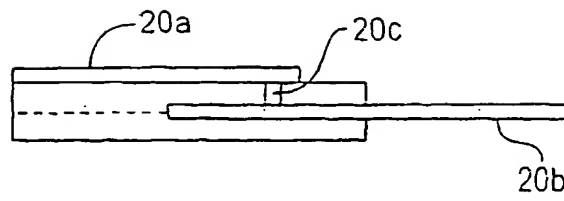


FIG. 3(b)

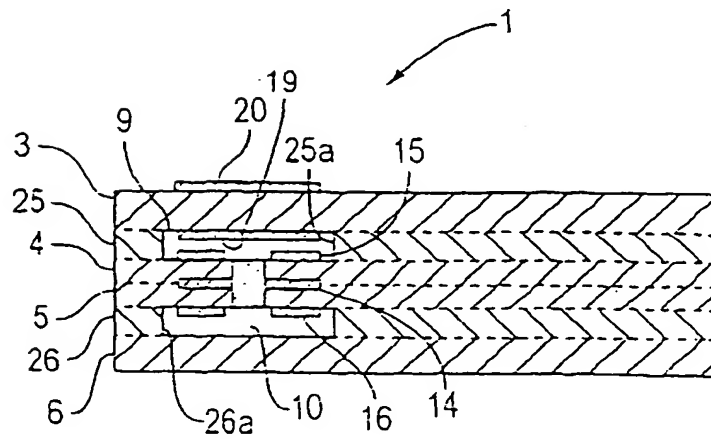




FIG. 5(a)

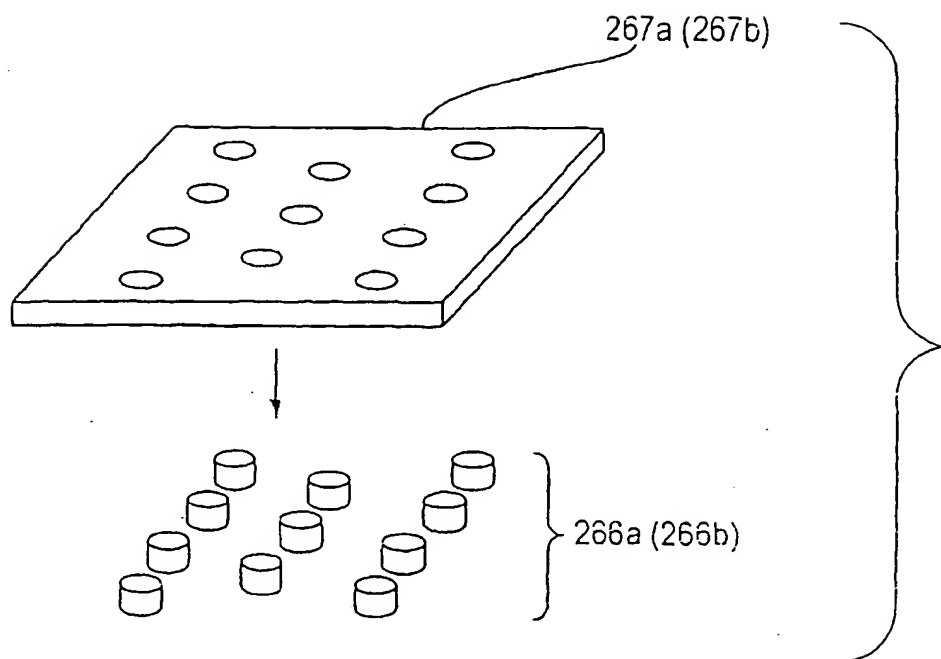


FIG. 5(b)

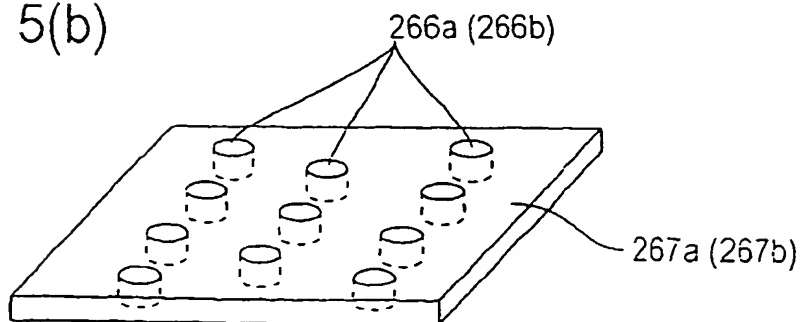


FIG. 7

55b

SECOND CELL ELEMENT				
ELECTROMOTIVE FORCE OF	E1	E2	E3	.....
CONCENTRATION CELL				
HC CONCENTRATION	C1	C2	C3	.....

FIG. 9(a)

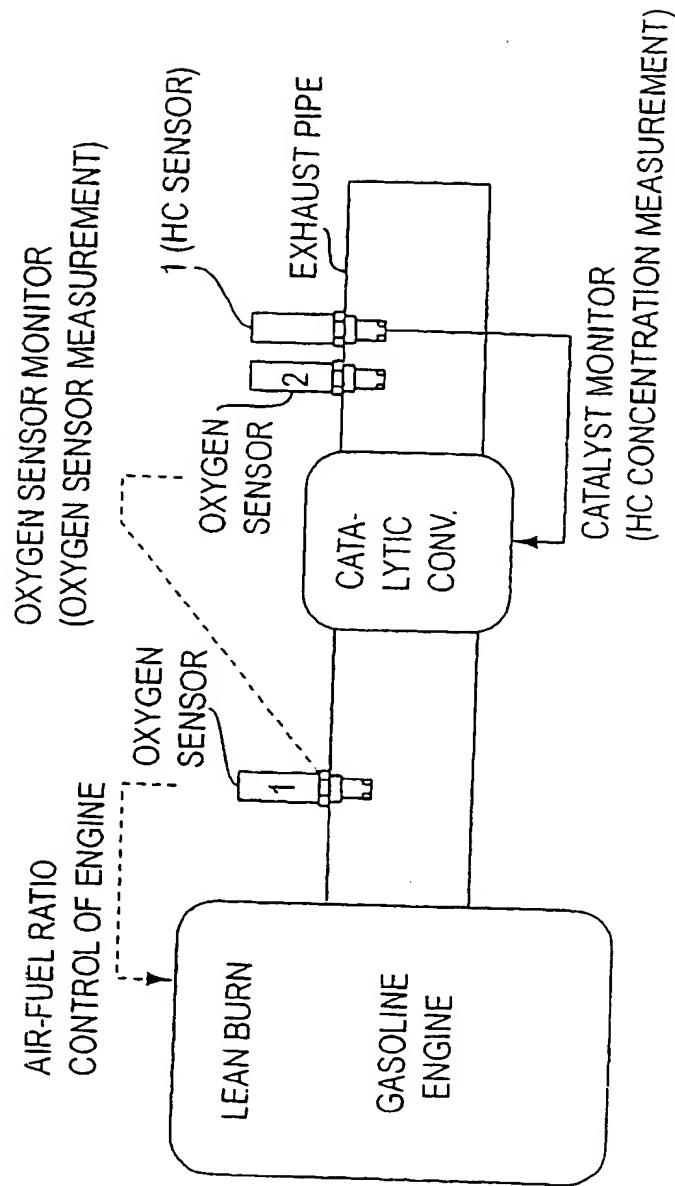


FIG. 10

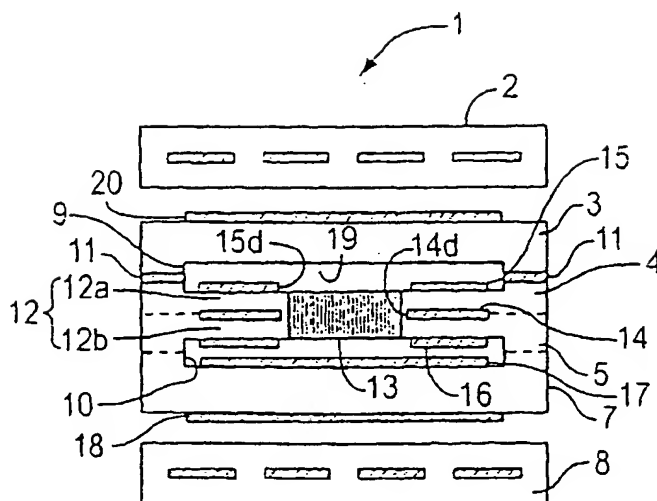


FIG. 12

$E_c = 550\text{mV}$   
( $P_x = 10^{-11}\text{atm}$ )  
GAS COMPOSITION:  $\text{CO}_2 = 10\%$ ,  
 $\text{H}_2\text{O} = 10\%$ ,  $\text{O}_2 = 7\%$ ,  $\text{N}_2$  BAL.

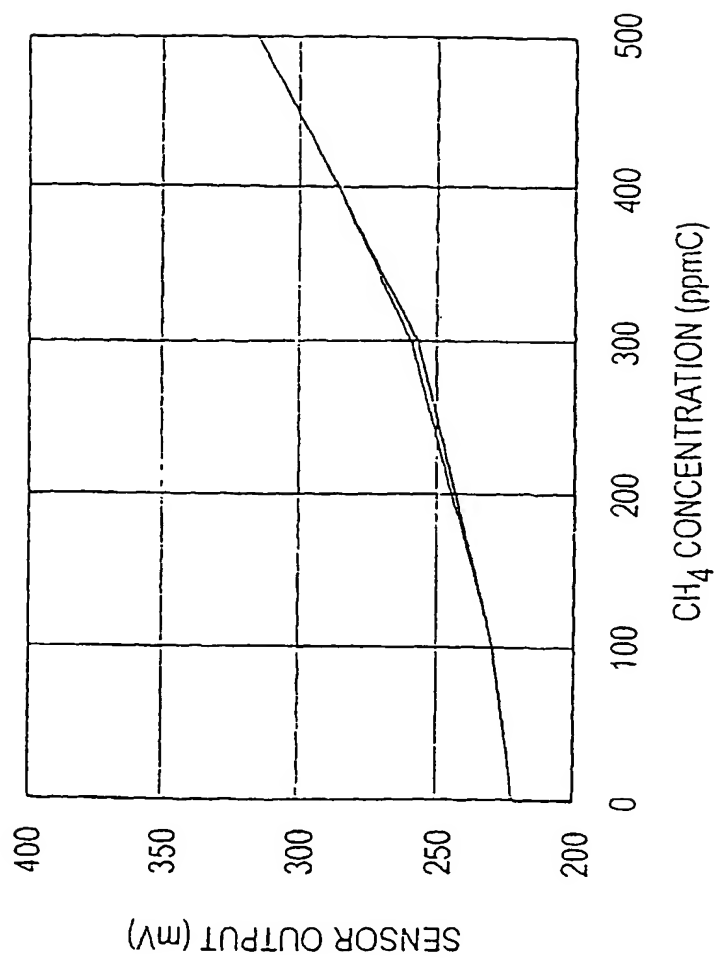


FIG. 14

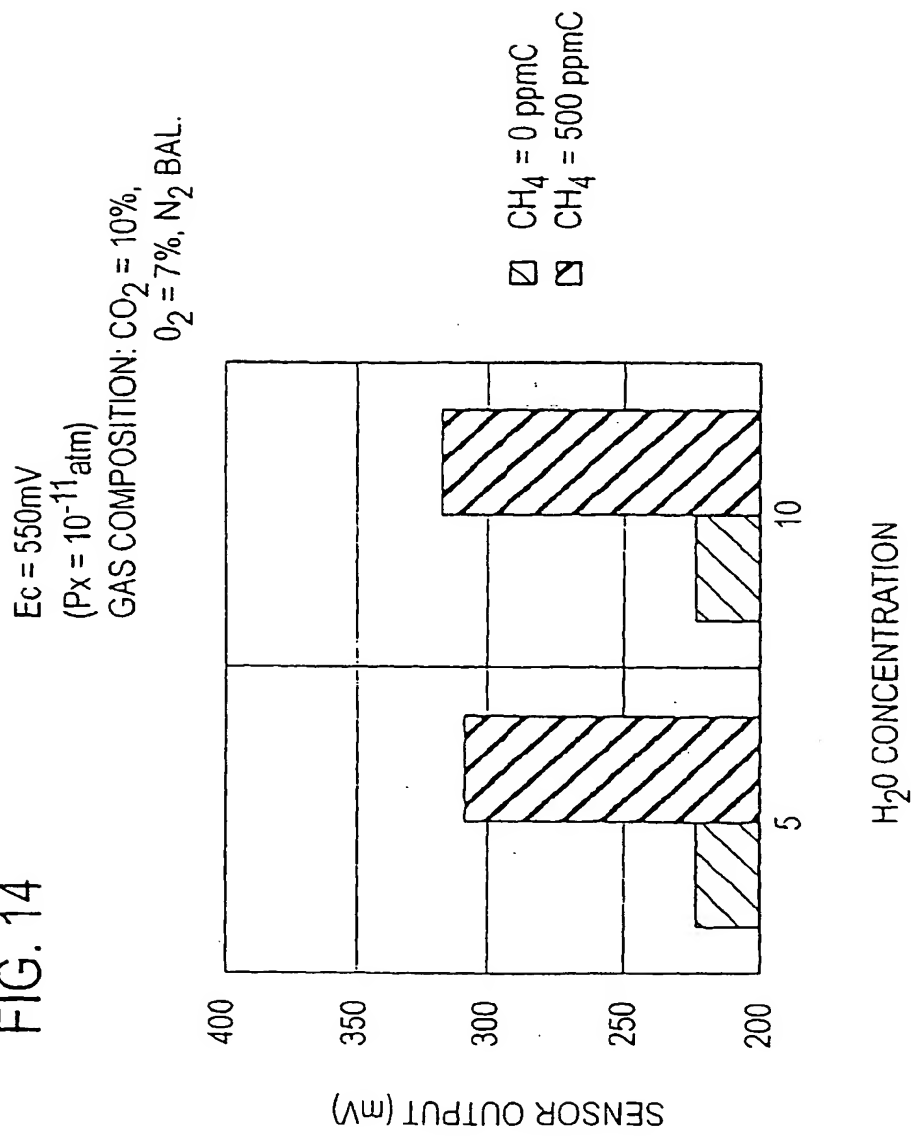
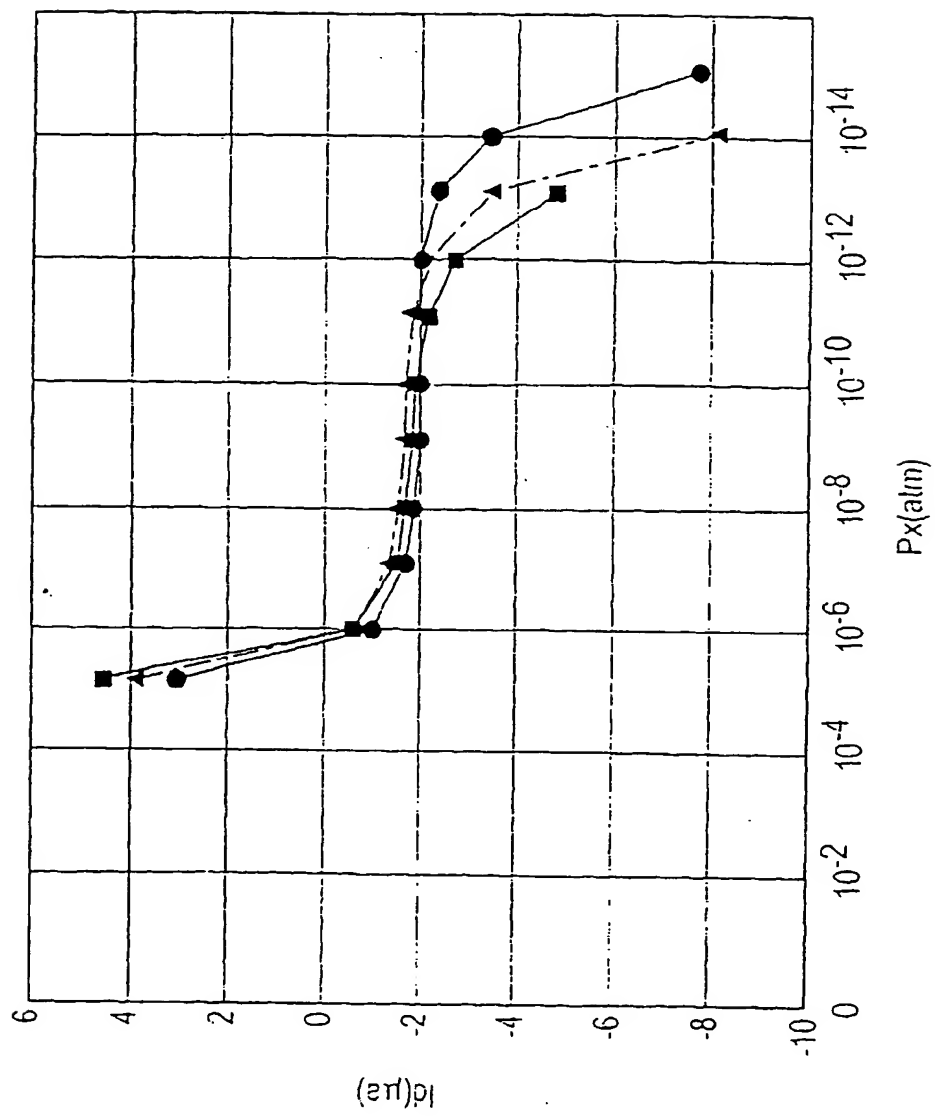




FIG. 16



H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub> DEPENDENCY  
E<sub>c</sub> = 550mV  
(P<sub>x</sub> = 10<sup>-11</sup> atm)  
GAS COMPOSITION: CO<sub>2</sub> = 10%,  
O<sub>2</sub> = 7%, N<sub>2</sub> BAL.

FIG. 18

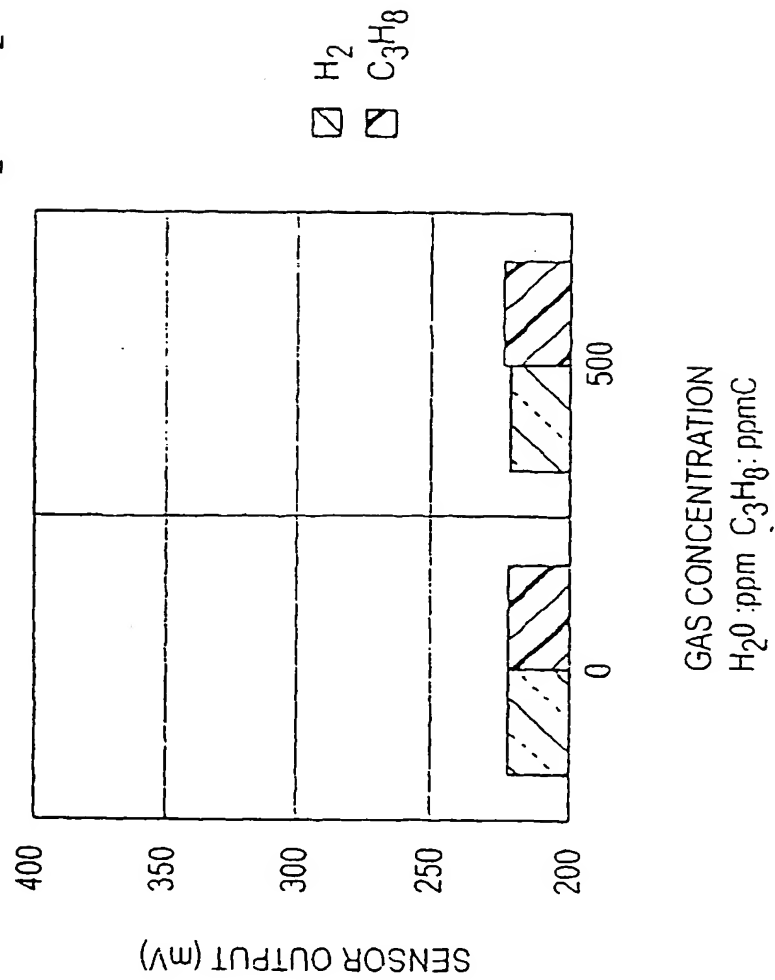


FIG. 20(a)

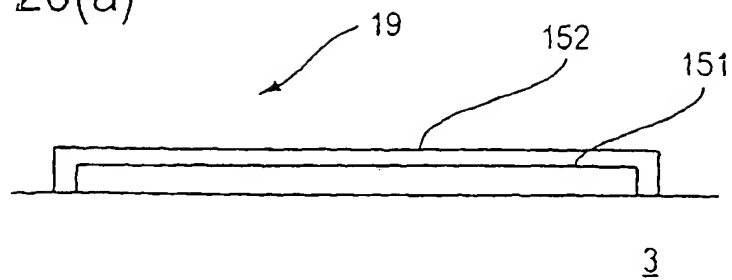


FIG. 20(b)

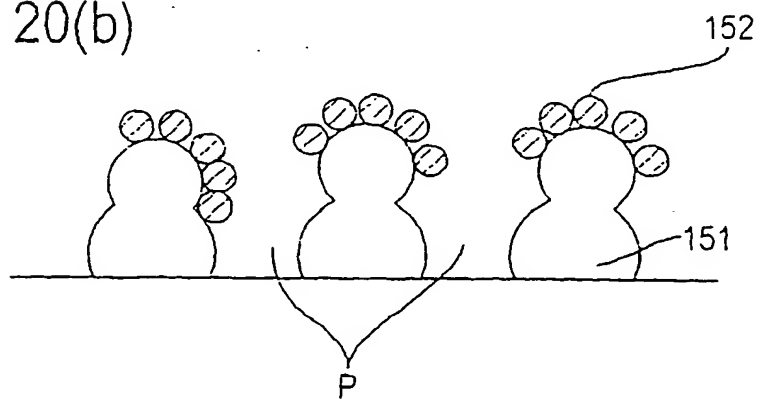


FIG. 20(c)

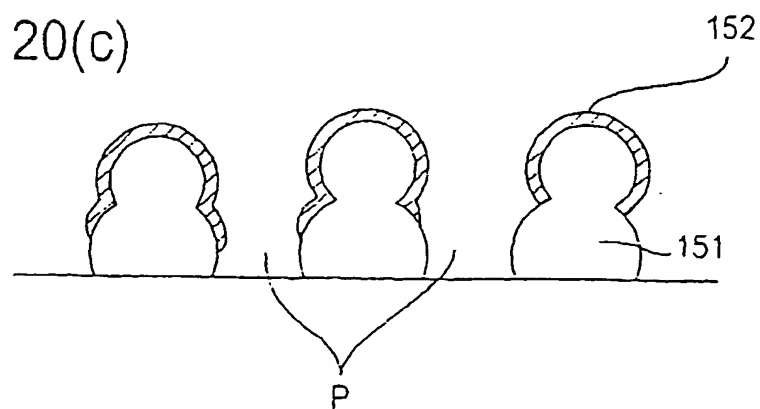


FIG. 22

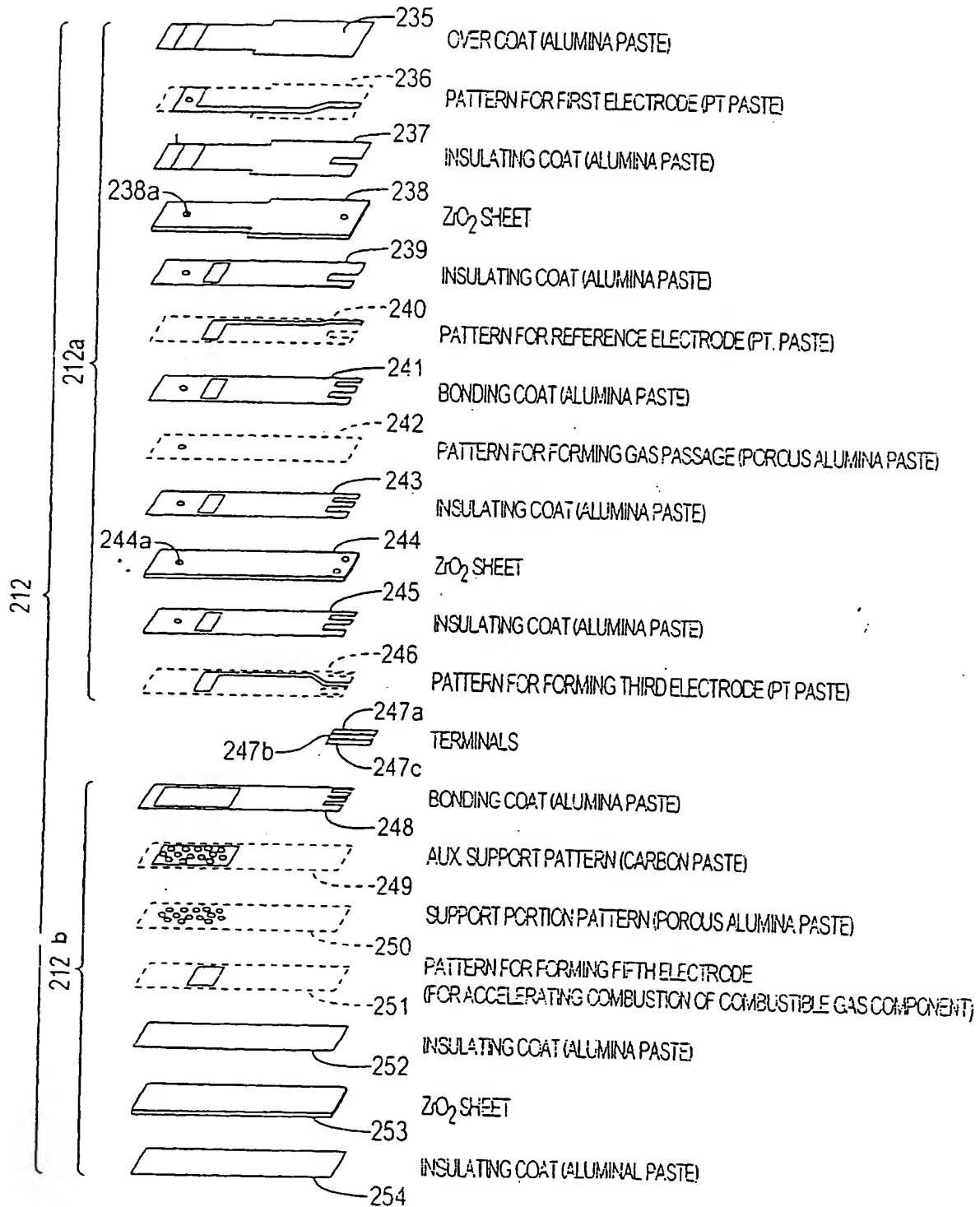
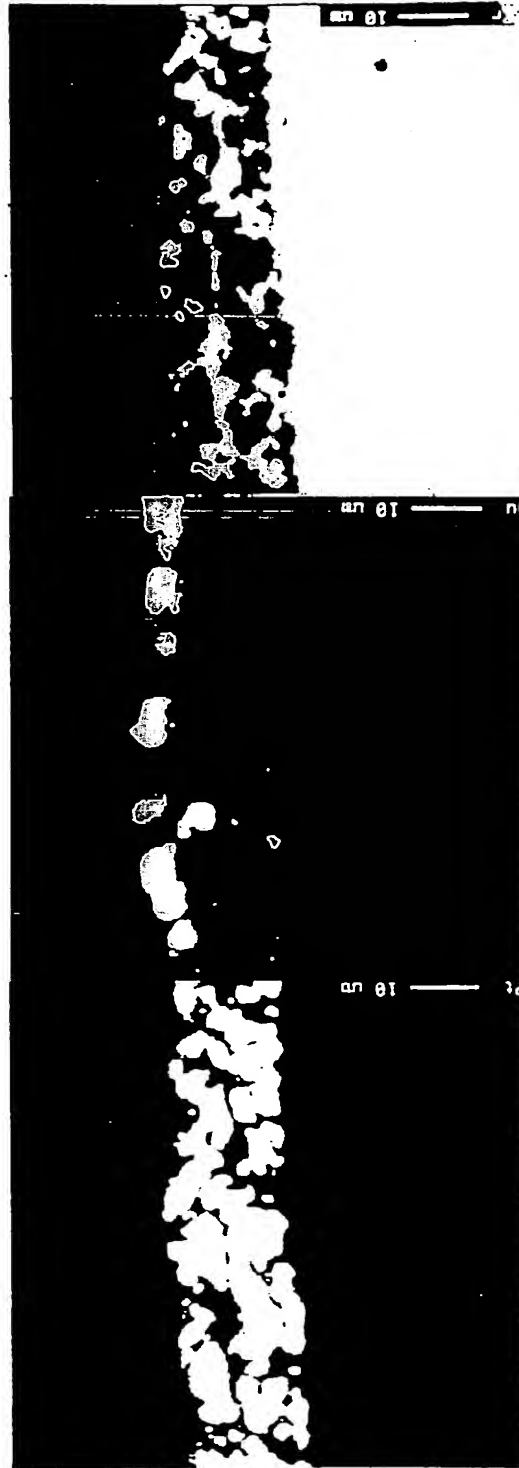


FIG. 24(a)      FIG. 24(b)      FIG. 24(c)



**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 11 7052

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
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08-12-1998

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